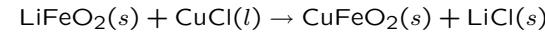
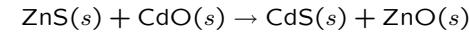
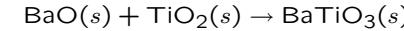
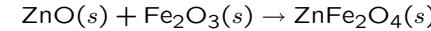
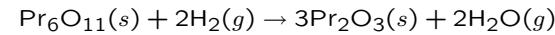
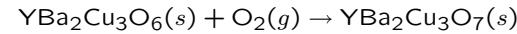


# Physics of Transition Metal Oxides

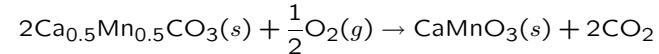
Lecture 13

Synthesis methods

Some of the typical reactions that occur in oxide synthesis:



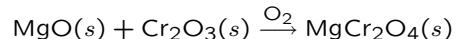
The thermal decomposition and oxidation steps usually take place at the same time



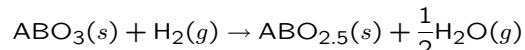
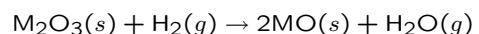
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Another route is to obtain a solid product from a gas phase reaction. MgO and Cr<sub>2</sub>O<sub>3</sub> do not react to form MgCr<sub>2</sub>O<sub>4</sub>, but Cr<sub>2</sub>O<sub>3</sub> reacts with O<sub>2</sub>, giving CrO<sub>3</sub>(g), which can react with MgO



Obtaining the correct phase often requires adjustment of the oxygen content. This can be done by annealing in a H<sub>2</sub>/N<sub>2</sub> mixture or a CO/CO<sub>2</sub> mixture. In simple cases annealing in argon or nitrogen may be sufficient. Hydrogen anneal would have the following effect:



where M is a metal, such as Fe.

Cation substitutions are also common. Typically this can be done if ionic radii match and charge neutrality is maintained. For example, partial substitutions can be made in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, replacing Y with Ca and Ba with La.

Ceramic synthesis

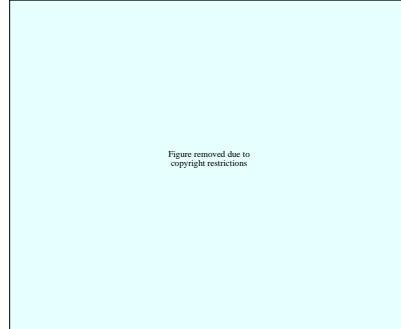
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Powders of oxide, carbonates, oxalates, etc. are mixed, possibly pelletized, and annealed. Annealing conditions are selected based on *phase diagrams*. Reaction usually occurs in an alumina, silica or platinum crucibles. If volatile components are present, reaction has to be performed in sealed capsules. Reaction temperatures are relatively high. Resistive furnaces go to about 1500°C, arck and skull heating up to about 3000°C and laser heating 4000°C or more.

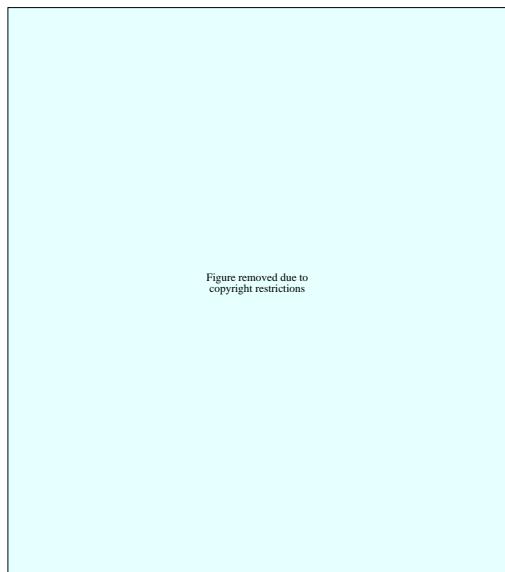
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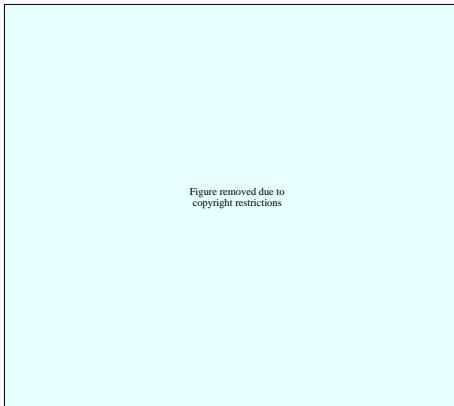
Phase diagrams can have quite complicated shapes when three or more elements are involved (plus oxygen). This is an example for  $\text{YBa}_2\text{Cu}_3\text{O}_{y-\delta}$  system.



Ternary phase diagram at  $850^\circ\text{C}$  and 1 atm.



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This shows the primary crystallization field for the YBCO 123 phase in greater detail. The phase labels are:

- 123 :  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$
- 211 :  $\text{Y}_2\text{BaCuO}_5$
- 101 :  $\text{Y}_2\text{Cu}_2\text{O}_5$
- 011 :  $\text{BaCuO}_2$

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### Problems with the ceramic synthesis technique

- If no melt forms during reaction, the whole process must happen in solid state and depends on very slow diffusion. Reaction starts at points of contact between constituents. Particles have finite size, reaction becomes slower as the reaction front moves deeper into particles.
- Only way to verify that the reaction has finished is to take periodic x-ray diffraction measurements or analyze the product in some other way.
- Difficult to guarantee a single-phase product.
- Different phases in the product are hard or impossible to separate.

Despite these shortcomings the technique is widely used and quite successful for cation substitution reactions.

Improvements can be obtained by smaller particle size ( $< 1\mu\text{m}$  instead of  $10\mu\text{m}$ ), e.g. by spray-drying, freeze-drying, coprecipitation.

### Precursors:

The diffusion length problem of solid-state reactions can be avoided if the necessary cations can be included in a suitable precursor. Oxide is formed by the decomposition of the precursor:

Precursor	Product
$\text{LaCo}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$	$\text{LaCoO}_3$
$\text{LaFe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$	$\text{LaFeO}_3$
$\text{Ba}[\text{TiO}(\text{C}_2\text{O}_4)_2]$	$\text{BaTiO}_3$
$\text{Li}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$	$\text{LiCrO}_2$
$\text{M}_3\text{Fe}_6(\text{CH}_3\text{-COO})_{17}\text{O}_3\text{OH} \cdot 12\text{C}_5\text{H}_5\text{N}$	$\text{MFe}_2\text{O}_4$ spinels

Many metals can be combined in a precursor by using carbonates.

Various carbonates have a similar calcite structure and can be readily prepared as solid solutions.

During heating in nitrogen or vacuum, an oxide  $\text{Mn}_{1-x}\text{MnO}$  is formed. The oxide has a rock salt structure. Metals that have been used include Mg, Mn, Fe, Zn, Ca, Co, Cd.

The simple oxides can be used as precursors for further synthesis.

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Examples of carbonate precursors:

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Examples of structures synthesized using mixtures carbonate precursors are shown here: (a)  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and (b)  $\text{Ca}_2\text{Mn}_2\text{O}_5$ . Both are oxygen deficient brownmillerites. Reaction temperatures are 1070 K and 1270 K.

More complex compositions can be made as well, such as the  $\text{A}_n\text{B}_n\text{O}_{3n-1}$  family, including  $\text{Ca}_2\text{FeCoO}_5$ ,  $\text{Ca}_2\text{Fe}_{1.6}\text{Mn}_{0.4}\text{O}_5$ ,  $\text{Ca}_3\text{Fe}_2\text{MnO}_5$ , etc.)

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A multistep synthesis route can be used to prepare perovskite-related  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$ .

The end members,  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{Ca}_2\text{Mn}_2\text{O}_5$  do not react in solid form ceramic synthesis.

Solid solutions can be obtained by

1. Starting with  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x(\text{CO}_3)_4$ .
2. Decompose in air at 1300 K, giving a perovskite  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_{6-y}$  ( $y < 1$ ).
3. The  $x = 0.67$  compound  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$ . This is an anion vacancy type  $\text{A}_3\text{B}_3\text{O}_{8+x}$  member of the  $\text{A}_n\text{B}_n\text{O}_{3n-1}$  family.
4. Reduce  $\text{Ca}_3\text{Fe}_2\text{MnO}_8$  in hydrogen, giving  $\text{Ca}_3\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ . Only  $\text{Mn}^{4+}$  is reduced,  $\text{Fe}^{3+}$  is unaffected.
5. Heat in vacuum at 1140 K and obtain the brownmillerite  $\text{Ca}_2\text{Fe}_{2-x}\text{Mn}_x\text{O}_5$

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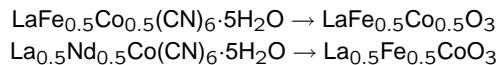
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Other precursors:

Hydroxides  $\text{Ln}_{1-x}\text{M}_x(\text{OH})_3$  with  $\text{Ln}=\text{La, Nd}$  and  $\text{M}=\text{Al, Cr, Fe, Co, Ni}$  and  $\text{Ln}_{1-x-y}\text{M}'_x\text{M}''_y(\text{OH})_3$  with  $\text{M}'=\text{Ni}$  and  $\text{M}''=\text{Co, Cu}$  crystallize in rare-earth trihydroxide structure and decompose at around 900 K, yielding  $\text{LaNiO}_3$ ,  $\text{NdNiO}_3$ ,  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ,  $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$ , etc.

Isostructural anhydrous alkaline earth nitrates  $\text{A}(\text{NO}_3)_2$   $\text{A}=\text{Ca, Sr, Ba}$  and  $\text{Pb}(\text{NO}_3)_2$  can be used to make solid solutions of  $\text{A}_{1-x}\text{Pb}_x(\text{NO}_3)_2$  type to synthesize  $\text{BaPbO}_3$ ,  $\text{Ba}_2\text{PbO}_4$ ,  $\text{Sr}_2\text{PbO}_4$ , etc.

Cyanides are also useful for synthesizing compositions that do not form as a result of ceramic reactions. Examples are



Less common precursors are metal alloys, e.g. an alloy of Eu, Ba, and Cu has been oxidized at 1170 K to produce superconducting  $\text{EuBa}_2\text{Cu}_3\text{O}_7$ .

Various other organometallic precursors are used in similar ways.

Topochemical reactions

Solid state reactions in oxides are often *topochemical*, i.e. the reactivity is controlled by the crystal structure, not the chemical nature of the constituents and involves the introduction of a guest (or removal) species into the lattice, resulting in significant structural modification.

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For example the dehydration reaction of  $\text{WO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$

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Oxide reduction reaction  $\text{ABO}_3$  to  $\text{A}_2\text{B}_2\text{O}_5$  are also topochemical. For example, reduction of  $\text{LaNiO}_3$  can results in members of a homologous series of compounds  $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$ . The most stable member of this series is obtained by controlled reduction in hydrogen at 600 K, yielding  $n = 2$   $\text{La}_2\text{Ni}_2\text{O}_5$ . This oxide can be reoxidized at a lower temperature. Note that  $\text{La}_2\text{Ni}_2\text{O}_5$  can not be formed by a solid state reaction of  $\text{La}_2\text{O}_3$  and a metal oxide.

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## Intercalation:

Insertion of a guest ion or molecule into a solid host lattice without major rearrangement of the solid structure.

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Typically happens in layered oxides where bonding within a layer is strong but weak between layers.

An example is Li intercalation in  $\text{TiO}_2$ ,  $\text{ReO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  or  $\text{Mn}_3\text{O}_4$ . Easy deintercalation of Li from  $\text{LiMO}_2$  is why these oxides are used in lithium cells.

Intercalation reactions can be used as a synthesis tools, e.g. lithium-intercalated anatase  $\text{Li}_{0.5}\text{TiO}_2$  transforms at 770 K into superconducting  $\text{LiTi}_2\text{O}_4$ .

We have already looked at alkali earth-intercalated  $\text{WO}_3$  and  $\text{MoO}_3$  phases.

## Examples of Li intercalation in oxide hosts

Host	Description
$\text{MO}_2$	$\text{Li}_x\text{MO}_2$ ( $x \geq 1$ ) M=Mo, Ru, Os, Ir. $\text{MO}_2$ has the rutile structure
$\text{TiO}_2$ (anatase)	$\text{Li}_x\text{TiO}_2$ ( $0 < x \leq 0.7$ ), converts irreversibly into a spinel $\text{LiTi}_2\text{O}_4$ at 770 K
$\text{CoO}_2$	$\text{Li}_x\text{CoO}_2$ ( $0 < x < 1$ ) various phases obtained by delithiating $\text{LiCoO}_2$
$\text{VO}_2$	$\text{Li}_x\text{VO}_2$ ( $0 < x < 1$ )
$\text{Fe}_2\text{O}_3$	$\text{Li}_x\text{Fe}_2\text{O}_3$ ( $0 < x < 2$ ) anion array changes from hcp to ccp
$\text{Fe}_3\text{O}_4$	$\text{Li}_x\text{Fe}_3\text{O}_4$ ( $0 < x < 2$ )
$\text{Mn}_3\text{O}_4$	$\text{Li}_x\text{Mn}_3\text{O}_4$ ( $0 < x < 1.2$ ) intercalation suppresses the tetragonal distortion
$\text{MoO}_3$	$\text{Li}_x\text{MoO}_3$ ( $0 < x < 1.55$ )
$\text{V}_2\text{O}_5$	$\text{Li}_x\text{V}_2\text{O}_5$ ( $0 < x < 1.1$ )
$\text{ReO}_3$	$\text{Li}_x\text{ReO}_3$ several phases depending on $x$

Hydrogen can be intercalated into various oxides.

Iodine has been intercalated into high-Tc oxides like  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$  without destroying superconductivity.

## Intercalation of water

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An unusual intercalation takes place during chemical oxidation of  $\text{Na}_{0.7}\text{CoO}_2$ . Water is incorporated in the lattice between the Na and  $\text{CoO}_2$  layers. During intercalation the  $c$  axis length increases from 10.96 Å to 19.62 Å. The in-plane lattice constant practically doesn't change. The final compound is  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$

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The intercalated oxide is superconducting with a  $T_c \approx 5$  K. A very unusual case of a Co-based superconductor. Superconductivity appears to be related to the isolated  $\text{CoO}_2$  layers, similar to the  $\text{CuO}_2$  layers in high-Tc cuprates.

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## Sol-gel synthesis

Sol-gel synthesis avoids the problems of powder ceramic synthesis. The process involves these (approximate) steps

1. Prepare a *sol*: a colloidal suspension of inorganic precursor in a liquid, such as alkoxyisilanes.
2. Adjust the pH of the solution to promote the formation of a *gel*
3. Dry the gel, forming a xerogel (or an aerogel or cryogel)
4. Sinter

Advantages of the sol-gel technique:

- Precursors are very finely mixed
- Relatively easy to adjust the stoichiometry
- Can be used for coatings, thin films
- Due to the small particle sizes, processing temperatures can be relatively low.

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## High-pressure synthesis:

### Up to 10 kbar

Moderately high pressures can be used in an open hydrothermal system, where reaction gas is under pressure ( $O_2$ ,  $N_2$ , etc.) Can be used for synthesis of  $RhO_2$ ,  $PtO_2$  (high oxidation state oxides).

Closed systems use an internal oxidant, like  $KClO_3$  which decomposes under reaction conditions providing the oxygen.  $RE_2M_2O_7$  compounds and zero thermal expansion ceramic  $Ca_{0.5}Ti_2P_3O_{12}$  can be synthesized this way ( $\approx 1000$  K, 3..5 kbar).

### 10 to 50 kbar

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Piston-cylinder type presses are used with integrated heaters. Temperatures of around 1800 K can be used. The pressure chamber may be made of tungsten carbide. Sample is in a metal capsule, sample size can be around 0.1 cm<sup>3</sup>.

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### over 50 kbar

Multianvil or belt piston presses can reach 150 kbar or more and very high temperatures of over 2000 K. Sample sizes are a few mm<sup>3</sup>.

High pressures are used for the synthesis of phases that would not otherwise form. The free energy is affected by the following processes

1. Pressure delocalizes outer  $d$  electrons by increasing orbital overlap
2. Pressure stabilizes higher valence states. For example, iron oxidizes to  $Fe^{4+}$  and it is possible to prepare  $CaFeO_3$ .
3. Pressure affects magnetic ordering and thus the electronic structure
4. Cations can enter different lattice sites under pressure. At ambient pressure we get a spinel  $A[AMn]O_4$  ( $A=Mg, Co, Zn$ ) because the  $2+$  ions prefer tetrahedral coordination. At high pressure the  $A^{2+}Mn^{4+}O_3$  phase forms where all ions are in octahedral sites.
5. High pressure stabilizes more close packed phases (higher coordination). These can occasionally be quenched to ambient pressure.
6. Solid state reactions are much faster under pressure (hours instead of days for  $LnFeO_3$ ,  $LnRhO_3$ ,  $LnNiO_3$ ).

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## The most traditional way for synthesizing oxides:

- mix constituent oxides, carbonates or other precursors
- heat
- grind
- check the phase that has formed by e.g. x-ray diffraction
- repeat heating and grinding if necessary

Often extreme environments are necessary: very high temperatures, high pressures, extreme oxygen partial pressures, rapid quenching, etc. This is the *brute force method*.

## Soft methods:

Typically some of the synthesis steps are done in solution phase. This includes dehydration, deintercalation (creating  $TiO_2$  from layered  $A_2Ti_nO_{2n+1}$   $A=Na, K, Cs$ ).

Electrochemical ion exchange techniques also belong to this group

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## Crystal growth

Most of the techniques discussed above result in powder samples. It is often necessary to obtain single crystals. The basic methods for that are

### Single component

1. Solid-solid
2. Liquid-solid
  - Directional solidification (Bridgman-Stockbarger)
  - Cooled seed (Kyropoulos)
  - Pulling (Czochralski and tri-arc)
  - Horizontal or vertical zoning
  - Flame fusion (Verneuil)
  - Slow cooling in a skull
3. Gas-solid (sublimation and sputtering)

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Growth from a melt is the most common technique.

(a) *Czochralski method*: Material is melted by an induction or resistance heater. The crucible needs to be nonreactive. The melt temperature is slightly above the melting point. A seed crystal is dipped into the melt and slowly withdrawn. Growth occurs at the interface. Can be used to grow very large crystals like  $\text{Al}_2\text{O}_3$ ,  $\text{LnAlO}_3$ ,  $\text{LnFeO}_3$ , garnets, etc.

(b) *Bridgman-Stockbarger*: A sharp temperature gradient in the melt induces nucleation and crystal growth

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(c) *Kyropoulos* similar to Czochralski method, but without pulling. Avoids exposure of the growth front to the atmosphere

(d) *Verneuil* powder is dropped into a flame, where it melts and drops onto the top of a crystal at the bottom. Similar to *plasma torch* method where a hot plasma is used instead of the flame

Growth from a solution is also widely used. In simple growth from melt (single component growth), the crystal grows due to a temperature gradient. In solvent growth (multicomponent), crystallization is driven by temperature-controlled supersaturation differences.

The solvent (or flux) technique is used to grow  $\text{BaTiO}_3$ ,  $\text{KTaO}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and many other oxides.

Flux materials (KCl, KF, PbO,  $\text{PbF}_2$ ,  $\text{B}_2\text{O}_3$ ) are often used to reduce the working temperature. The starting materials, dopants, and the flux is added into a crucible (or skull) and heated to melting point. After slow cooling the flux is poured away or etched away, leaving the crystals.

This is how various artificial gem stones (like ruby) are grown, starting at 1300 °C in a platinum crucible and cooling over a period of 3 months to 1000 °C.

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A variant of pulling is the *floating zone* technique, where a pressed rod of powder ceramic is heated in a narrow region. The powder melts in this region and recrystallizes.



This works in a similar way to *zone refining*.

The advantage of the floating zone and Verneuil methods is the lack of a crucible. These methods can therefore be used at very high temperatures and reactions with the crucible walls can be avoided.

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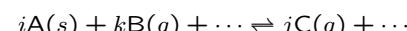
Also applies to the skull technique. Based on rf heating of a sample in a water-cooled copper enclosure. Slits in the copper allow the rf field to penetrate and heats the sample material. A thin solid layer remains in contact with the cold copper, i.e. the material makes its own crucible (the skull).

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Crystal growth from vapor

Physical vapor methods (vapor and solid have the same chemical composition). This includes sublimation and sputtering, for example.

*Chemical vapor transport* (CVT) relies on a chemical reaction in the gas phase



The carrier gas is responsible for moving material from the solid source to the crystal growth front. Temperature can be adjusted to enable crystal growth.

Starting material	Final product	Transport agent	Temperature (K)
$\text{SiO}_2$	$\text{SiO}_2$	HF	470 - 770
$\text{Fe}_3\text{O}_4$	$\text{Fe}_3\text{O}_4$	HCl	1270 - 1070
$\text{Cr}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{Cl}_2 + \text{O}_2$	1070 - 870
$\text{MO} + \text{Fe}_2\text{O}_3$ (M=Mg, Co, Ni)	$\text{MFe}_2\text{O}_4$	HCl	
$\text{Nb} + \text{Nb}_2\text{O}_5$	NbO	$\text{Cl}_2$	

CVT has been used to grow phase-pure  $\text{V}_8\text{O}_{15}$  (without other phases like  $\text{V}_7\text{O}_{13}$  or  $\text{V}_9\text{O}_{17}$ ). Transporting agents are  $\text{I}_2$ ,  $\text{TeCl}_4$ ,  $\text{Cl}_2$

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**References:**

Rao98 C. N. R. Rao, B. Raveau, "Transition Metal Oxides", Wiley, New York, 1998.